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XXVIII. *Analysis of the Moira Brine Spring near Ashby-de-la-Zouche, Leicestershire ; with Researches on the Extraction of Bromine.* By ANDREW URE, M.D. F.R.S.

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THE Moira coal mines are intersected by so many faults and slips, that they afford a very limited supply of water. The chief portion of the fresh water is drawn from within three hundred feet of the surface, by a pump barrel of nine inches diameter and six feet stroke, working four or five hours a day. It is raised at the rate of about seven strokes per minute, and amounts in this time to a volume of ninety-one gallons. There is a cistern at the bottom of the basset shaft connected with a reservoir cut in coal, which holds four or five days' drainage of water. The engine is employed in raising the fresh water not more than nine hours in a week.

The shafts for working the coal vary in depth from seven to eleven hundred feet. One shaft is 252 yards (or 756 feet) deep, and contains four lifts of pumps. The uppermost of these pumps delivers the water, which is altogether saline, into a cistern at the bottom of the basset shaft, whence it is raised from time to time. The average quantity of salt water alone employs the engine about eighty minutes daily, or ten hours in the week. The topmost lift of all the pumps delivers the water into a cistern about ten yards down the shaft: if the water comes from the fresh reservoir, it is allowed to run over at the top of the cistern down the drain into the brook; if from the salt reservoir, it is forced into the bath cistern by a forcing pump. The salt water is pumped up at the rate of five strokes and a half per minute, constituting seventy-one gallons per minute, whilst working, or about ninety hogsheads in a day.

In working the main coal, a little salt water oozes out; but this transudation, or bleeding as it is called, ceases after a time. In some few places small dribblings continue to issue, which collectively throughout the whole range of the Moira mines do not, in the course of twenty-four hours, exceed fifty hogsheads, and are conducted to the common reservoir.

The transudation of salt water generally appears in any adit in the coal as soon as driving commences. It slowly bleeds, but never spirts or springs forth as if from pressure; but its oozing is invariably accompanied with a faint hissing noise, as if air were escaping at the same time. The liquid proceeds chiefly from small crevices (pin-cracks), and seems associated with inflammable air, which separates as it trickles down the face of the coal. The gas is occasionally abundant enough to admit of being fired. In driving an adit in the solid coal to any distance, not so much as a dram of water is found at any one point, and very little oozes from the roof or floor

of the opening. When a lump of coal is detached, however, water soon afterwards begins to exude in drops from the crevices of the seam.

Immediately over the coal measures from which the saline water issues, there is a stratum of remarkably fine fire-clay, a shale free from iron and lime, called by the miners tow, about eighteen inches thick. This slate-clay is impermeable to water. Immediately under the coal lies a stratum of soft clay eight inches thick, which rests on a layer of compact slate-clay, several feet thick, also impermeable to water.

The bed of coal, although it contain pin-cracks which seldom extend many inches, has also the partings called slines, and those called cleavings in the direction of the bed; yet the coal is so little penetrable by water laterally, that it can confine by a wall a few yards thick the water of old workings.

When a fault has been perforated, water is seldom or never observed, so long as the confusion of strata occasioned by the break continues to exist. But from the parallel strata, the coal yields this saline water at almost every pore. The fault might have been a rent of an immense depth, but the line of slip is filled up and glazed, so to speak, by the incumbent pressure: hence in the greater number of instances where salt water is formed and continues to flow, the source of this fluid cannot be traced to the faults; for although near some of these the water may be abundant, yet generally the borders of the faults and the faults themselves are quite destitute of water, acting as barriers to it in every direction.

In consequence of the uniform distribution of saline matter through this coal, the potters are unable to employ it in their kilns, for it gives their earthenware the well known glaze due to the action of the vapour of chloride of sodium.

Saline water is found in one or more of the sandy rocks of the strata above the coal, but in very small quantity, and much less strongly impregnated than that which issues from the coal.

The brine-spring water is used for baths both at Moira and Ashby-de-la-Zouche as a medicinal application. These are celebrated for their sanatory powers in rheumatic, paralytic, and scorbutic diseases. Its internal administration, in small doses frequently repeated, is said to accelerate the discussion of scrofulous swellings, and of bronchocele; results which have been latterly ascribed to the combined agency of the bromides of sodium and magnesium with chloride of calcium which are found in the water.

A considerable quantity of this water was sent to me for analysis in bottles well corked and sealed*. Its taste is simply but strongly saline. It has no smell. It is pellucid and colourless. Its specific gravity at 60° FAHR. is 1.04647. A glass balloon being filled with it, the orifice was shut with a tight cork, from which a narrow bent glass tube proceeded, so as to dip under the mercury of a pneumatic trough. The balloon and tube were entirely filled with the water, to the exclusion of air. On the application of heat, gradually increased till the water began to boil, the air contained

* By EDWARD MAMMATT, Esq., superintendent of the mines and baths.

in it was disengaged, and received in a graduated tube over mercury. On examination it proved to be common air, with a slight excess of azote, equivalent altogether to only four and a half cubic inches in the gallon of water, or about one sixtieth part of the volume.

This quantity is not two thirds of the amount found in river water, nor more than half that in the waters of ordinary springs. The deficiency may be ascribed to the agency of saline matter in expelling air from water, in the process of solution, a fact particularly exposed in my paper on Nitric Acid published in the *Journal of Science* for January 1819.

One thousand grains of the water evaporated to dryness on a steam bath, afforded a group of saline crystals, which, after gentle ignition in a covered platinum capsule, weighed sixty-two and a half grains. During the ignition of the mother-water salts, a faint odour, resembling that of muriatic acid mixed with the hydrobromic, is perceptible.

As this water has its transparency hardly disturbed by nitrate of barytes, it obviously contains no appreciable quantity of sulphuric salts. In its concentrated state it does not affect solution of muriate of platinum, and therefore seems to be free from salts of potash.

Oxalate of ammonia indicates the presence of lime in notable quantity; and phosphate of soda applied to the liquid after the separation of the lime, detects magnesia by the peculiar aspect of the ammonia-magnesian phosphate. Tincture of galls shows the presence of a trace of iron; but ammonia added to the water occasions no appreciable precipitate of either that metallic oxide or alumina. From the slowness with which the iron is indicated by the galls, and the non-action of ferrocyanate of potash on the water even faintly acidulated, the iron is obviously in the state of protoxide. The quantity of chlorine present in a given weight of the water was determined by solution of nitrate of silver; and this amount was found to coincide with the weights of ignited chloride of sodium obtained by evaporation of the lime-free water, and of chlorides of calcium and magnesium inferred from the lime and magnesia got in the analysis. From the proportion of chlorine estimated by nitrate of silver, a small deduction must, however, be made on account of the quantity of bromine present, as determined by subsequent researches.

The following is the general result of the analysis of one gallon :

	Grains.
Bromides of sodium and magnesium	8
Chloride of calcium	851.2
Chloride of magnesium	16.0
Chloride of sodium	3700.5
Protoxide of iron	a trace
Solid saline contents in one gallon	4575.7

The above eight grains of bromides are equivalent to six grains of bromine.

Since the bromine is probably the most important ingredient of the Moira saline water, and since it is the one of which the quantity is most difficult to determine, I now proceed to offer some remarks on its elimination.

As bromine is always associated with chlorine in the waters from which it has been hitherto extracted, the first object of the analyst is to remove the chlorides as far as possible by crystallization. With this view the salts of lime and magnesia, which are usually present, ought to be decomposed at the outset by a due addition of carbonate of soda, so that the mother water obtained by evaporation may contain no deliquescent chlorides, but consist eventually of the chloride and bromide of sodium. By this precaution, also, none of the hydrobromic acid will be dissipated in the first process, as happens when the bromides of calcium and magnesium are present.

It is stated by MACQUER that chloride of sodium is insoluble in alcohol of specific gravity .840. I find, on the contrary, that a less aqueous alcohol, that of specific gravity 0.830, will dissolve at ordinary temperatures one twentieth of its weight of pure chloride of sodium; and that the same alcohol will dissolve fully five times as much bromide of sodium. On this difference of solubility in alcohol I sought to establish a simple method of separating the chlorides and bromides of sodium in the mother liquor of saline springs. On triturating with alcohol of 0.830 the saline mass obtained by evaporating the said mother liquor to dryness, a solution was obtained of specific gravity 0.985, which contained nearly one fifth its weight of saline matter, consisting chiefly of chloride of sodium. Thus it appears that a small proportion of bromide of sodium present in the alcohol, enables it to dissolve a large proportion of chloride. The separation of these two salts by alcohol is therefore impracticable.

The process which I eventually adopted for analysis, was to transmit through the mother liquor of the soda salts a current of chlorine gas till it communicated the maximum golden yellow tint, and then to pour in sulphuric ether, and agitate. The well known reddish yellow stratum of ether, combined with bromine and chlorine, soon rises to the surface of the saline solution. If the mother liquor has been submitted in its most concentrated state to the action of chlorine gas, the quantity of ether should be small in proportion to the bulk of the liquor; for if too much be added, it will hydrogenate the bromine, and cause the whole mass to become immediately colourless. If, on the other hand, the mother liquor be too dilute, it will absorb a quantity of chlorine proportional to its volume, whereby much ether will be decomposed. Distilled water made yellow by chlorine gas affords, on agitation with ether, a yellow supernatant stratum, not dissimilar to that produced by a minute portion of bromine treated in a similar way. It is therefore obvious that the reddish yellow ethereous stratum obtained from the mother liquors of bromic waters, is always a combination of chlorine and bromine with ether, in proportions more or less uncertain.

DESFOSSÉS or BERZELIUS * prescribes barytes as an agent for separating chlorine

* BERZELIUS, *Traité de Chimie*, i. 294.

from bromine, from the supposed property of chloride of barium being insoluble, and bromide of barium being soluble, in concentrated alcohol. I have digested in 60 times its weight of alcohol, sp. gr. 0·830, a mixture of chloride and bromide of barium, made by saturating the ethereous stratum with pure water of barytes, evaporating and igniting, and yet I found afterwards that much of the bromide had remained undissolved, evolving its ruddy vapour when acted on by manganese and sulphuric acid. Hence I cannot recommend this process to the analytical chemist.

Chemical research has two objects; the discovery of truth, and the improvement of the useful arts. The first object may, in the present instance, be attained with great precision by the followed method.

Having impregnated the mother liquor with chlorine gas, and agitated the dehydrogenated fluid with ether, separate the ruddy ethereous stratum by a funnel. More chlorine gas may now be transmitted through the liquor, and more ether may then be agitated with it, when usually a second layer of chloro-bromic ethereous fluid will be obtained, to be added to the former. Saturate exactly the ethereous liquid with a weak solution of pure soda, which may be done with extreme delicacy, in consequence of the loss of colour which instantaneously occurs whenever the neutral point is reached. In a few seconds a faint yellow tinge may reappear in the ether, which must be removed by a drop or two of the soda. The colour of bromine is as sensible a test of alkali as litmus. Separate the ether by a funnel, evaporate the sub-jacent saturated solution to dryness, and ignite carefully in a covered platina capsule. Weigh the mixed chlorides and bromides of sodium, and decompose ten grains, or any definite weight, of the mixture by solution of nitrate of silver. From the weight of the silver precipitate the relative proportions of the chloride and bromide present may be determined on the following principles:

10 grains of chloride of sodium are equivalent to 24·46 of chloride of silver.

10 grains of bromide of sodium are equivalent to 18·39 of bromide of silver.

Hence, if the silver precipitate from 10 grains be altogether a chloride, it will weigh 24·46 grains; and if altogether a bromide, it will weigh only 18·39 grains. The annexed Table will show that the differences of weight are sufficiently great for every analytical purpose.

Chloride of Sodium. Grains.	Bromide of Sodium. Grains.	Weight of Silver Precipitate.
10	+ 0	24·46
9	+ 1	23·85
8	+ 2	23·24
7	+ 3	22·64
6	+ 4	22·03
5	+ 5	21·42
4	+ 6	20·82
3	+ 7	20·21
2	+ 8	19·60
1	+ 9	19·00
0	+ 10	18·39

By a skilful application of analytical resources, differences ten times smaller than any represented by these numbers may be certainly appreciated in practice ; that is, the result may be found within one part in a hundred.

If 10 grains of the mixed salts be used for analysis by nitrate of silver, the following arithmetical rule will be found sufficiently accurate. From the number 24·46 deduct the weight of the silver precipitate, (perfectly dry of course,) and divide the remainder by 0·6 ; the quotient will denote the proportion of bromide of sodium present in the 10 grains of the mixed salts. Thus, supposing that 22·9 grains of silver precipitate have been obtained from 10 grains of a mixed chloride and bromide of sodium, the difference between 24·46 and 22·90 is 2·46, which, divided by 0·6, gives for a quotient the number 4·1, indicating four grains and one tenth of a grain of bromide of sodium. According to BERZELIUS, bromide of sodium has for its prime equivalent the number 101·7, hydrogen being unity, and consists of 78·39 bromine + 23·31 sodium.

I have been in the practice of solving many problems in analytical chemistry by the application of an arithmetical process analogous to the one above stated.

The chloride and bromide of silver are both soluble in water of ammonia, and cannot therefore be separated by this agent.

The best experimental mode of effecting the complete separation of bromine and chlorine in analysis may possibly be by converting the mixture of those two elements into perchloride and perbromide of mercury, and decomposing the perchloride by sulphuric acid. The perbromide is said to resist this powerful agent ; with what truth I have not ascertained. Red oxide of mercury dissolves when agitated along with water in the ethereous solution of bromine and chlorine, and affords a colourless solution.